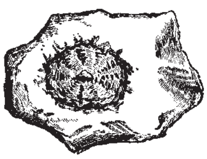
I have examined some of the stones under the microscope All have an air-bubble at the centre, and I thought in some I could distinguish a speck of sand or grit as well. The kernel appears to have infinitesimal cracks in the ice, going round the central bubbles in circles. Sometimes these are not spread out all round, but run up to the centre in spokes, widening out as they reach the edge. The dark line between the coatings appears to be composed of small pear-shaped air-bubbles lying with their narrow end towards the centre, and here and there in the ring are specks of grit or dust.

1.



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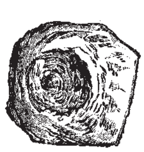

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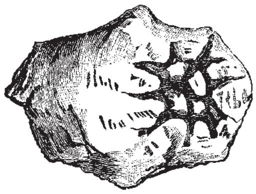

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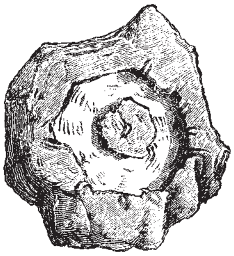

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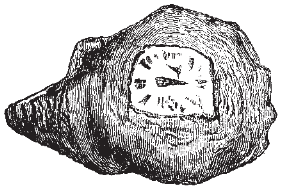

In the pear-shaped prominences the minute ice cracks appear to be formed in waving lines.

In some (Fig. 4), the air-bubbles are formed near the surface round the second or third layer, and are much larger; in others (Fig. 5), they appear in the kernel instead of the spoke-like formation of cracks. C. D. Holt.

Sefton Park, Liverpool.

Use or Abuse of Empirical Formulæ, and of Differentiation, by Chemists.

Prof. Thorpe's review of the work of Mendeleeff suggests to me a question I have several times previously thought of putting, viz. whether chemists are not permitting themselves to be run away with by a smattering of quasi-mathematics and an over-pressing of empirical formulæ. I do not make the accusation; I merely put the question as one suggested by an incomplete and superficial perusal of one or two recent memoirs.

To make my meaning clear, I will state a few facts, and if they are unnecessarily obvious I shall be glad to find them so.

Take percentage composition (p), and specific gravity (s); s is a function of p, and the question is, whether it is a continuous or a discontinuous function. To obtain an answer to this question, the best determinations of s should be plotted on a large scale in terms of p, with the probable limits of inaccuracy laid down, and then the curve should be examined to see whether it possesses, at the points of definite constitution, any kind of discontinuity, whether of slope or curvature. The answer may come out, either that such discontinuity certainly exists, or that it possibly exists, or that, if it exists at all, it must be below a certain specifiable order of magnitude. One of these is the definite kind of statement that can be made, and nothing else.

In order to assist the eye in forming a judgment, some form of mechanical integrator or differentiator might legitimately be run over the curve, provided due care were taken to avoid the creeping in of errors; but I doubt whether anything could be certainly detected in the derived curves that ought not to be visible in the original curve itself.

The process adopted by chemists seems a less satisfactory plan. I speak under correction. They assume some elementary form of empirical expression for the function, say a quadratic expression with three arbitrary coefficients, and they determine these coefficients to suit three points on the curve, first for one portion and then for another, taking these portions in the stages between one definite constitution and another; they thus obtain a set of quadratic expressions for s in terms of p, each with a more or less different set of coefficients: in other words, they find bits of parabolæ which more or less fit successive portions of the actual curve. They then differentiate each of these, and plot $\frac{ds}{dp}$, and they appear to be struck with the fact that, for each portion, these plottings come out precisely rectilinear; while with the observation that discontinuities exist between successive portions they seem quite pleased.

They sometimes go on to plot $\frac{d^2s}{dp^2}$, and to deduce fresh support for their facts by means of it.[1]

Now, were it not that eminent persons appear to lend their names to this kind of process, one would be inclined to stigmatize this performance as juggling with experimental results in order to extract from them, under the garb of chemistry, some very rudimentary and commonplace mathematical truths.

I would not be understood as casting any doubt on the *results* which may, by ingenious and clear-sighted persons, have been arrived at, even by so questionable a process: I would not be so understood, partly because those results lie out of my province, partly because the hypothesis of definite constitution for solutions or for alloys seems a very probable one, partly because I have myself plotted the s p curve for dilute ethyl alcohol, and clearly perceive the varieties of slope and curvature detected by Mendeleeff, though the changes are scarcely so sharp and definite at definite points as one might wish them to be in order to support the *a priori* improbable hypothesis of actual discontinuity. But what I want to assert, perhaps unnecessarily, is, that no juggling with feeble empirical expressions, and no appeal to the mysteries of elementary mathematics, can legitimately make experimental results any more really discontinuous then they themselves are able to declare themselves to be when properly plotted.

Liverpool, June 29. Oliver J. Lodge.

CHEMICAL AFFINITY.

In the older days, chemists were willing to think that, when they had said of a chemical occurrence, "It is a manifestation of the affinities of the reacting bodies," they had given a fair explanation of the occurrence. Nowadays, we rather avoid the term affinity. The modern chemist is not comforted by the word as his fathers were. Phrases, he knows, have a way of decoying a man to destruction. But, although he does not use the word affinity so much, the chemist is more eager than ever to understand the modes of action of affinity.

Since the latter part of the last century, the prevalent views regarding affinity have fluctuated between the doctrines of Bergmann and Berthollet. Bergmann taught that the causes of chemical action and gravitative attraction are identical; this cause being manifested, in one case, in an attraction between minute particles, and, in the other case, between comparatively large masses, of bodies. Further, he said that the result of chemical attraction between different kinds of particles is a change of composition wholly in the direction of the stronger attraction. Hence, according to Bergmann, substances may be arranged in the order of their affinities towards some standard substance. If A, B, and C are each capable of reacting chemically with D, and if the affinities of the three substances are in the order A, B, C, this means that addition of A to the compound BD, or to the compound CD, will cause the production of the new compound AD, and the liberation of B, or C.

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[1] Although Prof. Thorpe's review *suggested* the writing of this letter here is nothing contained in that review which prompts these remarks. Prof. Thorpe does not appear to have fallen into the errors which, in the writings of some chemists, I fancy I detect.

Berthollet, like Bergmann, regarded chemical affinity as an attraction between minute particles; but he asserted that affinity is conditioned by the physical properties of the attracting bodies, and also, and very specially, by the relative masses of these bodies. A relatively small attraction may overcome a greater, if the mass of one of the attracting bodies is largely increased relatively to that of the other. Berthollet's view is expressed by himself in the words, "Toute substance qui tend à entrer en combinaison, agit en raison de son affinité et de sa quantité."

These two conceptions still divide the allegiance of chemists. Berthelot's *law of maximum work* is the modern form of the Bergmannic doctrine. Guldberg and Waage's *law of mass-action* puts Berthollet's statement into exact form, and includes in its expression the conception of equivalency—a conception which has been developed since the days of Berthollet.

A great deal of work on chemical affinity has been carried on within the last few years. Ostwald has recently published a memoir of first-class importance. The present seems a good opportunity for endeavouring to give a sketch of the position of the subject.

The enunciation of Guldberg and Waage's law of mass-action, and of the *principle of the coexistence of reactions*, marks the beginning of the distinctly modern era of the study of affinity. The law of mass-action, first clearly put forth by the Norwegian naturalists in 1867, states that *chemical action is proportional to the product of the active masses of the substances which take part in the reaction.* The *active mass* of any member of a chemical system is defined to be the mass of that substance, stated in chemical equivalents, in unit volume of the system. Thus, if in a solution of hydrochloric acid, sulphuric acid, and caustic soda, the substances are present in the ratio

$$2HCl : H_2SO_4 : 2NaOH,$$

the active masses of the three substances are 1, 1, and 1 respectively, H_2SO_4 being taken as one equivalent of sulphuric acid. The investigations of Guldberg and Waage, and others, more especially of Ostwald, have shown that, if more than one member of a system is undergoing chemical change, each change proceeds as if it were independent of the other, and each substance obeys the law of mass-action. This statement is called by Ostwald the principle of the co-existence of reactions.

But the amount of chemical change which occurs when substances react is conditioned not only by the active masses of the substances, but also by their chemical nature, their states of aggregation, the temperature, and other variables. In their first memoir, Guldberg and Waage grouped these variables together under the name *coefficient of affinity.*

Let two substances, P and Q, react in solution to produce P′ and Q′, and let P′ and Q′ by their reaction re-form P and Q; let the active masses of P and Q be represented by p and q, and the active masses of P′ and Q′ by p' and q'; further, let the coefficient of affinity for the reaction between P and Q be represented by k, and the coefficient of affinity for the reaction between P′ and Q′ by k'; then the amount of decomposition of P and Q which occurs will be proportional to the product kpq; and the amount of decomposition of P′ and Q′ will be proportional to the product $k'p'q'$. When the equation $kpq = k'p'q'$ is fulfilled, the system will be in equilibrium.

The ratio k'/k is found by throwing the equation into the form—

$$(P - x)(Q - x) = k'/k\,(P' + x)(Q' + x);$$

where P, Q, P′, and Q′ represent the masses, stated in equivalents, of the four bodies initially present, and x represents the number of equivalents of P and Q which disappear, and also the number of equivalents of P′ and Q′ which are formed, when equilibrium results. Experimental measurements of P, Q, P′, and Q′, and x are required; from these the ratio k'/k is calculated, and, from this, values are found for x for different initial values of P, Q, P′, and Q′.

In their earlier treatment of the equation of equilibrium, given above, Guldberg and Waage spoke of the force which brings about the formation of P′ and Q′ being held in equilibrium by the force which brings about the re-formation of P and Q. The word *force* was used with a somewhat vague meaning, and certainly not with the meaning given to it in dynamics. Following the example of van 't Hoff, in their later memoirs the Norwegian naturalists regard chemical equilibrium as resulting when the velocity of the direct change—*i.e.* in the above case the change of P and Q to P′ and Q′—became equal to the velocity of the reverse change, *i.e.* in the above case the change of P′ and Q′ to P and Q. The equation of equilibrium arrived at by applying this conception is identical with that already given. By *velocity of the change* is to be understood the ratio of material chemically changed to time used in the change. Ostwald's analysis of the criterion of equilibrium, viz. that the velocities of the direct and reverse changes are equal when equilibrium results, is somewhat as follows. Let two bodies, A and B, be changed to A′ and B′; let the active masses of the four bodies, stated in equivalents, be p, q, p', q'; let x be the number of equivalents of A and B changed to A′ and B′, and the number of equivalents of A′ and B′ changed to A and B, at any moment; and let ξ be the value attained by x when equilibrium results; then

velocity of direct change $= (p - x)(q - x)c$; and velocity of reverse change $= (p' - x)(q' - x)c'$; and the velocity of the total change $= (p - x)(q - x)c - (p' + x)(q' + x)c'$.

Then $x = \xi$, and the velocity of the total change $= 0$, *i.e.* equilibrium results, when

$$(p - \xi)(q - \xi)c = (p' + \xi)(q' + \xi)c'.$$

This is the same equation as that given by Guldberg and Waage. But in this equation c/c' represents the ratio of the velocity-coefficients of the two parts of the change, whereas the ratio k/k' was called the ratio of the affinity-coefficients.

The simplest case in which to apply the above form of the equation of equilibrium is when A and B are caused to react in equivalent quantities without addition of A′ or B′; in this case $p = q = 1$, and $p' = q' = 0$, and the equation has the form

$$(1 - \xi)^2 c = \xi^2 c';$$

hence

$$\frac{c}{c'} = \left(\frac{\xi}{1 - \xi}\right)^2.$$

By determining ξ, *i.e.* the number of equivalents of A and B changed, and $1 - \xi$, *i.e.* the number of equivalents of A and B remaining unchanged, when equilibrium results, the ratio of the velocity-coefficients is found. This equation has been applied to varied classes of changes. Thomsen's measurements, by thermal methods, of the distribution of a base between two acids when one of the acids interacts with the salt of the base with the other acid, confirm the equation. Ostwald's measurements, by volumetric methods, of the same reaction which Thomsen examined by thermal methods, also confirm the equation. And the equation is confirmed by the determinations, made by Berthelot and P. de Saint Gilles by chemical methods, of the quantity of ethereal salt formed when an acetic acid reacts with an alcohol. The accuracy of the equation has also been confirmed by applying it to physically heterogeneous systems consisting of solids and liquids or gases; Ostwald (in his "Lehrbuch der Allgemeinen Chemie") gives the necessary forms of the equation for different cases.

The law of mass-action, and the principle of the coexistence of reactions, are thus amply confirmed. But the expressions, reaction-velocity, or velocity-coefficient, or coefficient of velocity, must be analysed.

The ratio $\left(\frac{\xi}{1 - \xi}\right)^2$ is called by Ostwald the *partition-coefficient* of the reaction. The square root of this ratio, *i.e.* $\frac{\xi}{1 - \xi}$, is the same as the square root of the ratio of the velocity-coefficients of the two parts of the change, *i.e.* it is the same as $\sqrt{\frac{c}{c'}}$; it is also identical with the ratio of the affinity-coefficients, k/k'.

When equivalent masses of one acid and the sodium salt of another acid interact in dilute solution, ξ represents the number of equivalents of the salt which are decomposed, and $1 - \xi$ represents the number of equivalents of the salt which remain unchanged, when equilibrium is established; or, to put the statement in another form, as each equivalent of salt decomposed produces one equivalent of acid and one of base, ξ represents the number of equivalents of base which have combined with the second acid, and $1 - \xi$ represents the number of equivalents of base which have remained in combination with the first acid. The ratio $\frac{\xi}{1 - \xi}$ then expresses the distribution of the base between the two acids. In the case of sodium sulphate (Na_2SO_4) reacting with nitric acid ($H_2N_2O_6$), Thomsen found $\xi = \frac{2}{3}$; therefore, the ratio $\frac{\xi}{1 - \xi} = \frac{2}{3}/\frac{1}{3} = 2$. In this case, the direct change consists in formation of sodium nitrate and sulphuric acid, and the reverse change consists in the re-formation of sodium sulphate and nitric acid; the square root of the ratio of the velocities of the direct and reverse changes in this reaction is $\frac{2}{3}/\frac{1}{3} = 2$. Or, one may say that the ratio of the affinity-coefficients of the acids nitric and sulphuric for the base soda is $\frac{2}{3}/\frac{1}{3} = 2$. These statements are identical. Two-thirds of the soda combines with the nitric acid, and one-third with the sulphuric acid, when equilibrium is established; or the velocity of the direct change is double that of the reverse change; or the affinity of nitric acid for soda is twice that of sulphuric acid for the same base. It must be remembered that the acids and the base interact in equivalent quantities and in dilute aqueous solution.

Proceeding in the way indicated by the foregoing example, Ostwald determined the ratio $\sqrt{c/c'}$, or k/k', for many acids reacting with a given base; he stated these ratios in terms of one acid taken as 100. For instance, taking the base soda (Na_2O) the ratio for $\frac{H_2Cl_2}{H_2SO_4}$ was found to be 1·94, for $\frac{H_2N_2O_6}{H_2SO_4}$ 2·0, and for $\frac{H_2Cl_2}{H_2N_2O_6}$ ·97. If the affinity of nitric acid for soda is taken as 100, that of hydrochloric acid for the same base, according to these results is 97, and that of sulphuric acid is 50. Ostwald examined many different experimental methods for measuring the distribution of a base between two acids in dilute solution. The experimental difficulties are great, and the results obtained by one method cannot be expected to agree very closely with those obtained by another. Secondary reactions very often complicate the change which it is sought to measure. The order of the affinities of many acids, for a specified base, was not altered by a change of method, except in a few cases: in these cases the affinities were very small, and therefore incapable of accurate measurement by any of the methods tried.

Ostwald next proceeded to examine the influence of the nature of the base on the affinities of acids. He showed that whether the base be potash, soda, ammonia, magnesia, zinc oxide, or copper oxide, the ratio of the affinities of hydrochloric and nitric acids is the same; but that the ratio varies in the case of sulphuric and hydrochloric, or sulphuric and nitric, acids. But it is known that sulphuric acid reacts with its normal sodium salt to form an acid salt ($NaHSO_4$); Ostwald was able to explain the results obtained with sulphuric acid on the supposition that the affinity of this acid for a base, as measured by any of the methods used by him, really represents only the affinity of that part of the acid which has not combined to form an acid salt. He concluded that the true relative affinity of sulphuric acid, like the affinities of hydrochloric and nitric acids, is independent of the nature of the base. Extending the investigation to other acids, Ostwald concluded that the relative affinities of the acids are independent of the nature of the bases with which they react, and can be expressed by constant numbers. If this conclusion is accepted, it follows, from the nature of the reaction examined, that the relative affinities of the bases are also independent of the acids with which they react, and can be expressed by constant numbers. From these conclusions, the further deduction is made that the affinity between an acid and a base is the product of two specific affinity-coefficients, one of which belongs to the acid and the other to the base.

This conclusion is of extreme importance and requires rigorous examination. In order to test the accuracy of the statement that each acid has a specific affinity-coefficient, Ostwald has determined the affinities of a series of acids by different methods, with the result that the affinity-coefficients determined by one method are as nearly the same as those determined by other methods as could be expected, considering the errors inherent in the methods themselves. If each acid possesses a specific affinity-coefficient, the value of this coefficient for any acid might be expected quantitatively to condition many, if not all, the reactions brought about by that acid. Several chemical changes brought about by acids, other than those in which an acid interacts with the salt of another acid, have been examined by Ostwald. Among these changes may be mentioned that of acetamide to ammonia and acetic acid, that of methylic acetate to acetic acid and methylic alcohol, and that of cane-sugar to inverted sugar. The rate of each of these changes varies according to the acid added to the system; the results obtained show that the square roots of the ratios of the velocity-coefficients are in the same order as, and are as nearly identical as could reasonably be expected with, the ratios of the affinity-coefficients of the acids employed, as determined by the division of a base between these acids. Hence the conclusion that each acid has a specific affinity-coefficient is verified, and at the same time new methods for determining these coefficients are put into the hands of chemists.

But none of the methods employed was found altogether satisfactory. In every case secondary reactions more or less interfered with and complicated the primary change.

There is, however, another and altogether different method whereby the affinities of acids may very accurately be determined. This method is based on the relations which certainly exist between the rate of a chemical change brought about by an acid and the electrical conductivity of an aqueous solution of that acid. If the electrical conductivities of dilute aqueous solutions of a number of acids are stated in terms of that acid which has the greatest conductivity taken as unity, and the numbers so obtained are compared with the relative affinities of the same acids determined by one of the methods already described, a very close parallelism is noticed between the two series of numbers. By carefully studying the effect of dilution on the conductivities of monobasic acids, Ostwald has arrived at the conclusion that the dilutions at which the molecular conductivities of monobasic acids exhibit equal values bear a constant relation to each other. For instance, the molecular conductivity of monochloracetic acid at any dilution is equal to that of butyric acid when the solution of the latter is 256 times more dilute than that of the former acid. By *molecular conductivity* of an acid is meant the conductivity of a solution of a quantity of the acid proportional to its molecular weight. If μ = molecular conductivity, and λ = electrical conductivity, as ordinarily defined, stated in mercury units, then $\mu = 10^7 n\lambda$, where n = number of litres to which the molecular weight of the acid taken in grammes is diluted.

The conductivities of the stronger monobasic acids, such as nitric, hydrochloric, chloric, vary but little with dilution; the maximum values are reached in moderately dilute solutions. The conductivities of the weaker acids, such as phosphoric, acetic, butyric, however, vary much with dilution, and increase very considerably as dilution increases. The rate of increase varies; as a rule, the weaker the acid the greater is the increase for a specified dilution. The maximum values are not the same for all acids. Ostwald's investigations show that the affinity of an acid is closely connected not so much with the maximum conductivity of a solution of that acid as with the rate of increase of conductivity relatively to the maximum conductivity. To determine the affinity of an acid, by the electrical method, it is, therefore, necessary to determine the molecular conductivity of an aqueous solution of that acid at varying dilutions until the maximum conductivity is reached.

But it is very difficult, if not impossible, to determine directly the maximum conductivity of a solution of a weak acid, because when very much water is present the unavoidable impurities in the water affect the conductivity more than the minute quantity of acid which is present. Ostwald has found that the maximum conductivity of a monobasic acid in solution can be calculated from determinations of that of the sodium salt of the acid, and moreover that the maximum conductivity of the sodium salt can be calculated from the observed conductivities at different dilutions. The method by which these results are arrived at cannot be gone into here; suffice it to say that it is based on an extension and modification of the generalisation made by Kohlrausch, to the effect that the conductivity of an aqueous solution of a normal salt of a strong monobasic acid is the sum of two constants, one of which depends only on the nature of the acid, and the other only on the nature of the base.

The further application of the electrical method to find the affinity-coefficients of acids rests to a large extent on the extension made by Arrhenius to electrolysis of van 't Hoff's *law of osmotic pressure*. The law asserts that equal volumes of solutions of definite substances, at the same temperature and osmotic pressure, contain equal numbers of molecules, which numbers are the same as would be contained in equal volumes of gases at the same temperature and pressure. The law has been verified in different directions; it cannot, however, be accepted as a final statement. One conclusion drawn from the law of van 't Hoff, by thermodynamical reasoning, is that solutions of definite substances in the same solvent which have the same freezing-point exert equal osmotic pressures at their freezing-points; and hence, solutions which contain equal numbers of molecules in equal volumes, and which therefore exert equal osmotic pressures, have the same freezing-point. This deduction is identical with the *law of molecular lowering of freezing-point*, empirically established by Raoult. This deduction, if granted, enables the osmotic pressures of solutions to be calculated from observations of the freezing-points of these solutions; the calculated pressures can then be compared with those determined by direct experiment. There are many apparent exceptions to the law of molecular lowering of freezing-point, and to the law of van 't Hoff. Arrhenius explains the exceptions by supposing that the substances in question are partially dissociated in aqueous solution, and that therefore a specified volume of one of such solutions contains a greater number of molecules than would be the case if dissociation had not occurred. This explanation rests on the analogy between the gaseous state and the state of substances in dilute solution. As the pressure of the vapour obtained by heating ammonium chloride is greater than that calculated by Avogadro's law on the assumption that the vapour consists of molecules of NH_4Cl, but as the observed pressure agrees with the calculated pressure when the vapour is assumed to consist of equal numbers of molecules of NH_3 and HCl, so the apparently abnormal osmotic pressures of many solutions may be reconciled with the law of Van 't Hoff by assuming that the compounds in these solutions are more or less dissociated into simpler molecules. Substances which are not (by hypothesis) dissociated in aqueous solution are generally, if not always, non-electrolytes. The exceptions to the law of van 't Hoff occur chiefly, if not wholly, among electrolytes. Ostwald, following Arrhenius, supposes such electrolytes to be more or less dissociated into their ions in aqueous solutions.

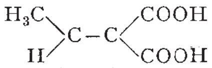
As this hypothesis of electrolytic dissociation rests on the identity of the laws expressing gaseous dissociation and dissociation in solution, it follows that generalisations made regarding gaseous dissociation may be applied to dissociations in solution. Suppose that a gaseous substance is dissociated into two gases; let the pressure of the undissociated portion be p, and the pressure of the dissociated portion be p_1; then, at constant temperature, the relation of p to p_1 is expressed by the equation $\frac{p}{p_1^2} = c$. Again, the pressure of a gas at any specified temperature is proportional to its mass, u, and inversely proportional to its volume, v: now, as the osmotic pressure of an undissociated compound in solution, according to the law of van 't Hoff, is equal to the pressure which the same mass of that compound would exert if it existed as a gas occupying the same volume as is occupied by the solution, the osmotic pressure in the solution, p, may be put as proportional to $\frac{u}{v}$; therefore, from the equation already given, $\frac{uv}{u_1^2} = C$.

Let μ_∞ = molecular conductivity of a binary electrolyte at infinite dilution, and let μ_v = conductivity of v litres containing one molecular weight in grammes of the electrolyte; then, the fraction μ_v/μ_∞ expresses the molecular conductivity at any stated dilution referred to the maximum conductivity, and on the hypothesis of electrolytic dissociation the same fraction expresses the portion of the electrolyte which is dissociated in terms of the whole quantity of the electrolyte taken as unity. If this fraction is expressed by u_1, and if u represents the undissociated portion of the electrolyte, we have $u = 1 - \mu_v/\mu_\infty$. If now we put $m = \frac{\mu_v}{\mu_\infty}$, and substitute in the equation $uv/u_1^2 = C$, we have $\frac{1 - m}{m^2}v = C$. This equation states that $\frac{1 - m}{m^2}v$ must have the same value for all dilutions of any one binary electrolyte; a statement which is amply confirmed by the researches of Ostwald. The constant C obtained by applying the above equation to a monobasic acid represents the affinity of that acid. The constant C measures the readiness of an aqueous solution of the acid to conduct electricity, as also its readiness to take part in chemical reactions; the value of C depends only on the nature of the acid, and is independent of dilution. As C has small values for strong acids and large values for weak acids, Ostwald prefers to put the equation in the form $\frac{m^2}{(1-m)v} = k$, where $k = \frac{1}{C}$. To avoid small fractions Ostwald multiplies m, and also k, by 100; he has determined $100k$ for more than 100 monobasic acids at dilutions varying from 8 to 1024 litres; finally, he expresses the most probable value of $100k$ as K. I cannot here give even a selection from the numerous measurements of K made by Ostwald, but must content myself with drawing attention to some of the conclusions he has come to regarding connexions between the affinities and the constitution of acids. The method has been worked out chiefly for monobasic acids.

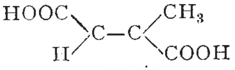
In the acetic series of acids, affinity decreases from formic to propionic acid, and then remains nearly constant until caproic acid is reached. The substitution of chlorine or bromine for hydrogen in an acetic acid raises the affinity, bromine causing a smaller increase than chlorine. If S is substituted for O in the group COOH in acetic acid, the value of K is raised from ·0018 to ·0469; while the substitution of the group SH for H in the same acid is attended with an increase in the value of K from ·0018 to ·0225 only. The greater or less acidic character of such groups as OH, OCH_3, OC_6H_5, NO_2, &c., is quantitatively measured by the increase in the value of K attending the substitution of one of these groups for H in an acid. In the acetic acids, the change of H to OH is accompanied by an increase of affinity, OCH_3 is more acidic than OH, and OC_6H_5 is the most acidic of the three radicles considered. In studying the relations between the affinities of acids and their derivatives, attention must be paid not only to the composition and character of the replacing groups, and to the series of acids in which the replacement occurs, but also to the position of the replacing groups relatively to the other atoms of the molecules. The influence of position is very marked in the affinities of the isomeric oxy, chloro, nitro, methoxy, and acetoxy, benzoic acids. The following numbers exhibit the influence of the positions of the replacing groups:—

		K.
$C_6H_3 . COOH . OH . OH$	1 : 2 : 3	·114
,, ,,	1 : 2 : 6	5·0
$C_6H_5 . COOH$		·006
meta—$C_6H_4Cl . COOH$		·0155
ortho— ,, ,,		·132
meta—$C_6H_4NO_2 . COOH$		·0345
ortho— ,, ,,		·616
ortho—$C_6H_4 . OC_2H_3O . COOH$		·0333
para— ,, ,, ,,		·00422
ortho—$C_6H_4 . OCH_3 . COOH$		·00815
para— ,, ,, ,,		·00302

It is seen that the group OCH_3, or OC_2H_3O, substituted for H in benzoic acid, raises the affinity, if the group is placed in the ortho-position, but decreases the affinity if the group is placed in the para-position. The influence of the position of the replacing groups on the change of affinity of many acids points to some connexion between the affinities of acids and the space-arrangement of the atoms which form the molecules of the acids; measurements of the affinities of such acids as maleic and fumaric, mesaconic, citraconic, and itaconic, confirm this conclusion. Maleic acid is about twelve times stronger than fumaric acid; these acids are probably geometrically isomeric, and the COOH groups are probably nearer one another in maleic than in fumaric acid. Again, if the formulæ of Wislicenus for citraconic and mesaconic acids are adopted we should expect the former to be the stronger of the two. These formulæ represent the acids as geometrically isomeric; they are—


citraconic

and


mesaconic

The values obtained for K are, for citraconic ·34, for mesaconic ·079: the third isomeride, itaconic, is very weak; K = ·012.

Ostwald's researches open up a new path along which advance may be made: they show us how to connect the characteristic property of an acid, its affinity, with the constitution of the acid; they form a further and more important step towards solving *the* problem of chemistry, which is to find definite and measurable connexions between the properties and the composition of homogeneous kinds of matter.

But the coefficient of affinity of an acid has not yet been fully analysed. What is the meaning of the constant K? What is affinity? The value of K for a monobasic acid measures the readiness of that acid in solution to take part in chemical changes, and also the readiness of an aqueous solution of that acid to conduct electricity. Now, when a compound is electrolysed, the parts or ions into which it is separated are chemically equivalent and carry with them equal quantities of electricity, and the electricity travels only with the ions. The conductivity of the electrolyte will depend on the number of molecules electrolysed, and on the velocity of transference of the ions across the space separating the electrodes. The greater the number of molecules separated into ions, and the more rapid the migrations of these ions, the greater will be the conductivity of the substance. Hence the value of K for an acid will be conditioned by the amount of separation into ions, and the rate of migration of these ions; *i.e.* the affinity, as well as the conductivity, of the acid will depend on these quantities. The ions into which a monobasic acid is separated when electrolysis occurs are H and a negative radicle; the scheme of electrolysis may be represented as $HR = H + R$. As hydrogen moves much more rapidly than the most rapid negative acidic ion, the molecular conductivity of a monobasic acid in solution is chiefly conditioned by the degree in which the acid is separated into its ions. The affinity of the acid is sometimes dependent to a considerable extent on the velocity of the negative ion: in such cases acids which are separated into their ions to an equal extent will exhibit different affinities; in other cases the degree of electrolytic separation is the chief factor conditioning the affinity. Now the fact that, so far as accurate research has gone, electrolytes fully obey Ohm's law, or, in other words, the fact that the smallest electromotive force suffices to cause electrolysis, points to the action of the E.M.F. in electrolysis as being only a directive action on the ions already existing. This view of electrolysis has been developed by Clausius, and recently by Arrhenius, van 't Hoff, and Ostwald. The hypothesis, in its present form, bids us regard an aqueous solution of an electrolyte as already more or less completely dissociated; it bids us see the molecules of the electrolyte in the solution as dissociated into their ions; it says that the electrolytic and the chemical activity of the solution is dependent on the ratio between the number of dissociated, or "active," molecules, and the number of undissociated, or "inactive," molecules. This view of electrolysis, and of chemical change occurring between electrolytes, regards an aqueous solution of a strong acid as containing a great many free ions, which are, respectively, hydrogen and a negative radicle; it looks on an aqueous solution of a weak acid as containing only a few free ions.

There are difficulties in the way of accepting the hypothesis of electrolytic dissociation. At first sight one is shocked by being told that a very strong acid such as nitric acid, or a very strong base such as potash, is dissociated in aqueous solution, to perhaps 90 per cent., into its ions; in the case of potash, one remarks that the ions must be potassium and the group OH, and that each of these bodies reacts with water the moment they are brought into contact. To meet these objections, Ostwald reminds us that a chemically energetic compound is one which readily suffers chemical change, and the parts of which are therefore readily separated; and he remarks that the *ion* potassium is not the same thing as ordinary potassium; the ion holds a large electric charge; when it comes to the electrode it gives up this charge, and *then*, but not till then, it reacts with water. But difficulties still remain: one of the greatest is to explain the mode of action of the solvent. Does the solvent merely form a medium in which the separate ions move about? Why then does increase of solvent increase the amount of dissociation? May not the solvent react with the dissolved body to form complex molecular aggregates which then dissociate into simpler ions? Is the dissolved body the electrolyte, or is the electrolyte a compound, or aggregate, made up of the dissolved body and the solvent? Is the electrolyte actually separated into its ions in the solution, or does it only exhibit an "aptitude for directed dissociation"? These questions, and questions such as these, have yet to be answered.

The hypothesis of electrolytic dissociation has been worked out in detail in several directions, by Arrhenius and Ostwald, and has been found to give results in keeping with experiment. In considering its application to explain chemical change between electrolytes—for it really presents a theory of chemical changes between electrolytes—it is necessary to remember that, in its present form at any rate, it is applicable only to substances in aqueous solution. Because a solution of hydrochloric acid is very chemically active, it does not follow that liquid HCl should also be chemically energetic; nor, because gaseous HCl is not dissociated by heating to a fairly high temperature, does it follow that an aqueous solution of this compound should not be largely dissociated into the ions hydrogen and chlorine.

The hypothesis of chemical change between electrolytes in solution, which is based on van 't Hoff's extension of the law of Avogadro to substances in dilute solutions, and on the general close agreement between such dilute solutions and gases, cannot yet be finally accepted or rejected by chemists. It has already done much to draw closer the connexions between chemical and electrical phenomena, it has gone further than any other hypothesis of chemical change in helping forward the solution of the main problem of chemists, and it has opened up many new lines of advance.

There is one general conclusion to be come to from the study of all the recent work on chemical affinity: I think we may agree with Ostwald when he says that Bergmann was certainly right in assigning a definite affinity to each element and compound, and that Berthollet was right in asserting that affinity is modified by the relative masses of the reacting bodies, but that Bergmann erred in saying that chemical change always occurs in one direction only and that the direction of the strongest affinities, while Berthollet also erred in regarding the affinity between acids and bases as inversely proportional to the equivalent weights of the reacting compounds. Bergmann's error has been revived in modern times; it has now assumed a physico-chemical aspect; it finds its expression in Berthelot's so-called *law of maximum work*, which asserts that every chemical change accomplished without the addition of energy from without tends to the formation of that body or system of bodies the production of which is accompanied by the development of the maximum quantity of heat. In so far as this statement can be translated into precise terms it can be proved to be dynamically unsound. When applied to chemical reactions, it tells us that of several possible reactions that one which is accompanied by the production of the greatest quantity of heat occurs to the exclusion of others; but this has again and again been experimentally disproved.

M. M. PATTISON MUIR.

THE PASTEUR INSTITUTE.

LAST week the Lord Mayor received a letter from M. Pasteur, acknowledging receipt of the resolutions passed at the recent Mansion House meeting. In this letter M. Pasteur writes:—

"If the aphorism that science has no country has never received authoritative sanction, it did so at this meeting, in which the leading *savants* in biological and medical science of the United Kingdom took part. I wish I could thank them individually for having attended this gathering. I was filled with gratitude on learning that the Prince of Wales himself had accorded his high approbation of your initiative. Modesty compels me to pass over in silence the kind words of which my labours and those of the Pasteur Institute have been the subject, but I have a right to rejoice with all friends of the progress of humanity at the great moral effect of the meeting. The manifestation of July 1 had not only for its object the question of the treatment and possible extinction of hydrophobia in England, but in the nature of things it was also a protest against that false sentimentality which led certain persons, not—which was already a strong point with them—merely to put on the same footing the life of men and that of animals, but even to prefer the existence of animals to the salvation of human life. When this view is taken, what is the limit? We must become firm vegetarians. We must even extend our scruples so that no living being is sacrificed. We must endure the importunities of a mosquito, the daring of a mouse, the stings of a flea—false ideas or excuses for a tirade which one finds is most often at the bottom of all the attacks on experimental physiology. Certain credulous souls—by I know not what tales—imagine that our laboratories are chambers of torture. They ignore the fact that the rabbit or the guinea pig is rendered insensible by chloroform before it is subjected to the most insignificant operation. As for me personally, the suffering of an animal affects me so much that I would never shoot a bird, and the cry of a wounded skylark pierces me to the heart; but if the investigation of the mysteries of Nature and the acquisition of new truths be at stake, the sovereignty of the object justifies all. Who, then, having the least regard for the pursuit of the knowledge of the mysteries of Nature, would put in the balance the sacrifice of a few fowls and rabbits with the discovery of the attenuation of virus and prophylactics which have resulted from such sacrifice? No one, my Lord Mayor, will have contributed more than you have done to rectify the errors which under a show of compassion can only hinder the progress of science and compromise even the most legitimate interests of humanity."

THE TERRESTRIAL GLOBE AT THE PARIS EXHIBITION.

SOME time before the opening of the Paris Exhibition it was announced that one of the attractions of the show would be a great terrestrial globe, one millionth of the actual size of the earth. This globe is now exhibited in a building specially erected, near the Eiffel Tower, for the purpose, and it excites the warmest interest among all visitors who have devoted the slightest attention to geographical science. It was designed by MM. Villard